

# CALIBRATION CURVE FOR GPC ANALYSIS OF ASPHALTS

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## INTRODUCTION

A better understanding of the structure of asphalts is important not only for scientific purposes, but also from the technological and economic viewpoints because this binder is used in very large quantities in road construction. Research workers therefore seek to acquire in-depth knowledge of this binder, making it possible to relate compositional parameters to practical properties. Among the physical and chemical analysis techniques capable of contributing to the characterization of such a medium, gel permeation chromatography (GPC) is a good choice because of its efficiency and its ease of application. Further, the development of finely graded subgrades has added to the preceding advantages that of a response time of the same order of magnitude as that obtained with gas chromatography.

The application of GPC to the characterization of heavy petroleum residues has already been dealt with in a certain number of publications. Among these mention may be made of the work of Altgelt (1,2) on the scatter range of the molecular weights of asphaltenes and maltenes, that of Richman (3) and of Bynum and Traxler (4) on the qualitative characterization of road asphalts. The problems raised by molecular weight calibration were investigated by Albaugh et al. (5) as well as by Dickson et al. (6,7). Snyder (8) studied the problems involved in the application of analytical GPC to asphalt characterization and demonstrated that, unlike polymers, the response of refractometric and ultraviolet detectors was not independent of elution volume. Reerink and Lijzenga (9) have proposed a molecular weight calibration method based upon the comparison of results obtained by ultracentrifugation. Significant experimental work involving fractionation of asphalt by preparative GPC and the characterization of fractions by analytical GPC, viscosimetry, vapor pressure osmometry, infrared and nuclear magnetic resonance spectrometry have been published by Kiet et al. (10).

All of this work has demonstrated that the quantitative interpretation of GPC asphalt chromatograms raises two types of problem. The first, that of correcting the response of the detectors, has been dealt with in earlier publications (11,12). The second, relative to the establishment of a calibration curve in molecular weight, is dealt with in the present paper.

## FRACTIONATION OF ASPHALTS BY PREPARATIVE GPC

To plot a calibration curve in GPC the best approach consists in injecting a sufficient number of standards having a chemical structure and make-up identical to those of the product to be characterized. If these standards do not exist, they must be prepared and characterized. We have thus used preparative GPC to isolate a sufficient number of narrow fractions of asphalts of various origins. The classical conditions of a preparative fractionation are given below:

- Apparatus: Waters Chromatoprep 101
- Columns: 2 columns ( $10^3$  and  $10^4$  Å), diameter 5 cm, length 120 cm
- Solvent: redistilled chloroform
- Flow rate: 20 ml/min
- Injected volume: 100 ml

- Injected solution concentration : 10 %
- Volume of fractions : 125 ml.

The efficiency of the fractionation is evaluated by the injection, in analytical GPC on two micro-Styragel columns of  $10^3$  and  $10^4$  Å, of 0.3 mg of the most representative fractions. Figure 1 shows the chromatograms of the fractions 6 to 18.

It is noted that, apart from the heaviest fractions (fractions 6, 7 and 8) for which the behavior is special and which represent less than 1 % of the initial product, the preparative separation is indeed carried out according to the molecular weight. A calculation of the average characteristics carried out on the largest fraction (fraction 16) leads to the following numerical values :  $M_n$  (in equivalent polystyrene) = 555,  $M_w$  (in equivalent polystyrene) = 690. The polydispersity is thus 1.24, which can be regarded as satisfactory.

#### CALIBRATION CURVE BY VAPOR PRESSURE AND MEMBRANE OSMOMETRY

The determination of the number average molecular weights - either by vapor pressure osmometry (VPO) or by membrane osmometry - of the asphalt fractions obtained by preparative GPC makes it possible to establish a first experimental relationship between elution volume (in analytical GPC) and molecular weight. Most of the measurements were performed by means of a Mechrolab 301A vapor pressure osmometer. Some determinations were carried out, for the fractions of high molecular weight, with a membrane osmometer of the same make. The measurements were conducted in benzene at 37°C on solutions with concentrations varying between 20 and 5 g.l<sup>-1</sup>. It was thus possible to determine the number molecular weights of preparative GPC fractions of four asphalts, namely two 80/100 samples (ELF Feysin and ELF Grandpuits) and two 40/50 samples (Shell and CFR). The representative points of the molecular weight as a function of distribution coefficient are given in Figure 2. The values of the molecular weights corresponding to the points located in the upper part of the curve ( $M_n$  higher than 10,000) were obtained by membrane osmometry. This figure also shows (continuous bold line) the calibration curve in molecular weight plotted for polystyrenes.

It is noted that the experimental points, although obtained from four asphalt samples having different crudes and manufacturing processes, describe a single curve. This calibration curve, specific to asphalts, is not very different from the polystyrene curve for distribution coefficients between 0.5 and 0.7. Beyond these values, the asphalt curve moves either toward the largest elution volumes, for the same molecular weight, or toward the higher molecular weights, for a given elution volume. It can be noted that the lower part of the curve (weights lower than 1000) which corresponds to substances of high aromaticity, moves substantially away from the polystyrene curve, probably owing to the superposition of an adsorption process which increases as the aromaticity of the products increases and as their molecular weight decreases. For molecular weight values higher than 10,000, we shall see in the discussion of the viscosimetric measurements that part of the shifting can be explained by the fact that the molecular weight is determined on non-ideal solutions.

#### INTRINSIC VISCOSITY OF ASPHALT FRACTIONS

The viscosimetric measurements were carried out in THF at 30°C by means of an FICA automatic dilution viscosimeter. The sample analyzed is a CFR 40/50 asphalt which we fractionated under classical conditions. Figure 3 shows the experimental points corresponding to the variation of the expression  $(t-t_0)/t_0.C$  as a function of the concentration  $C$  of the solution ( $t$  being the solution flow time and  $t_0$  the solvent flow time).

This figure shows that, unlike what is observed in the case of ideal solutions, the relationships are not linear for the high molecular weight fractions except beyond a concentration of the order of 2 to 3 g.l<sup>-1</sup>. Below this value, the curves bend downward in proportion to the molecular weight. This illustrates the dissociability of the species as a result of dilution and the existence of a critical concentration beyond which the solutions have a "normal" behavior. The intrinsic viscosity values determined by extrapolation, to zero concentration, of the linear part of the curve are thus apparent values which take into account a partially associated state. As the molecular weights measured by vapor pressure osmometry or membrane osmometry were determined on solutions whose concentration was higher than the critical concentration indicated by viscosimetry, we conclude that, here too, what is involved is the apparent molecular weights taking into account the associability of the species.

#### CONSTRUCTION OF $[\eta] M$ CURVE OF ASPHALTS

The numerical values of intrinsic viscosities and molecular weights make it possible to plot the curve  $[\eta] M = f(Kd)$  for 40/50 CFR asphalt fractions. This curve is shown in Figure 4 together with the universal calibration curve (continuous bold line). The dotted line is the calibration curve in  $[\eta] M$  proposed by Reerink and Lijzenga (9) for asphaltenes.

The discrepancy between the curve in  $[\eta] M$  established for asphalt fractions and the universal calibration curve is qualitatively of the same order as that which was observed in the calibration of molecular weight. It may be considered that the observed deviation in the lower part of the curve is due to the elution lag caused by adsorption of aromatic substances of low molecular weight. For fractions with high molecular weight we have shown that the numerical values of intrinsic viscosity and molecular weight were apparent values higher than the real values because the measurements were not carried out on ideal solutions but on solutions whose concentration was higher than the critical value. The product  $[\eta] M$  thus measured is hence greater than that which is obtained in GPC.

#### CALIBRATION CURVE USING UNIVERSAL CALIBRATION

As the micellar behavior of solutions of asphalt fractions of high molecular weight leads to apparent values during the determination of molecular weight by membrane osmometry, it is difficult to plot a calibration curve in molecular weight of asphalts by traditional means. Under these conditions, we have assumed - as a working hypothesis - that the universal calibration of Benoit et al. (13) is applicable to asphalt fractions. The use of universal calibration in the case of GPC on micro-packings calls for continuous measurement of the viscosity of the eluate. It was Ouano (14) who first substituted for the measurement of a flow time that of the pressure drop at the terminals of a capillary tube. The principle was taken up by Lesec (15) who demonstrated that the measurement of the pressure at the inlet of a capillary tube placed between the outlet of the columns and the inlet of the refractometer could be interpreted in terms of viscosity. We therefore set up the viscosimetric detector described by Lesec and formed a capillary tube of 0.23 mm diameter and 3 m length. A branch at the inlet of this capillary allows pressure measurement. A data acquisition system permits the processing of data from the detectors by computer.

After calibrating the analytical GPC system in terms of hydrodynamic volume by means of polystyrene standards, we fractionated the asphalts (four samples of 180/200, two of 80/100, two of 60/70 and two of 40/50) under usual conditions for preparative GPC. Each fraction was analyzed by analytical GPC with viscosimetric detection in order to determine its intrinsic viscosity under the real conditions of the GPC. Its molecular weight was then determined by reference to the universal calibration curve.

We also used VPO to determine the number average molecular weights for the fractions of small molecular weight which have an ideal behavior in solution. All the measurement points are shown in Figure 5 in which we have reproduced the calibration curve for polystyrenes (bold line) and the calibration curve in molecular weight of asphalts previously established by membrane osmometry (thin line).

It is noted that these measurements make it possible to define a new calibration curve in molecular weight for road asphalts, a calibration curve which is independent of the origin of the crude and of the manufacturing process. This curve is much more realistic than that established by membrane osmometry because it is plotted by measuring the intrinsic viscosity by GPC with viscosimetric detection, but its validity is limited by the hypothesis initially made regarding the applicability of the universal calibration to asphalt fractions. It is also seen that this curve moves further away from the curve for polystyrenes and molecular weight increases, thus verifying the classical hypothesis that the compactness of heavy asphalt fractions increases with molecular weight.

In order to utilize this new calibration curve easily, we compared the calibration curve for asphalts with the calibration curve for polystyrenes. The relationship obtained is shown in Figure 6.

The adjustment of this relationship on a second-degree equation leads to the following expression:

$$\log Y = 3.21 - 1.04 X + 0.331 X^2$$

in which Y = asphalt weight and X = polystyrene weight.

Furthermore, we deemed it of interest to compare the values of intrinsic viscosity and of molecular weight obtained by GPC with the results published by Altgelt (16), on the one hand, and Kiet et al. (10) on the other hand. The different relationships  $\log |\eta| = f \log (M)$  are given in Figure 7.

Fairly good agreement is found for the low molecular weights, and then significant bending of the viscosity curve obtained by GPC with viscosimetric detection.

#### CONCLUSION

The work reported in this paper shows that it is possible to approach experimentally the problem of the plotting of a calibration curve in molecular weight for GPC on a micro-packing applied to the characterization of asphalts. It is shown that if one determines, for different asphalts, a specific calibration curve relating the number average molecular weight, measured by membrane osmometry, of narrow fractions to their elution volume, one obtains a single curve independent of the origin of the crude and of the manufacturing process. This curve is very close to the polystyrene curve for values between about 1000 and 3000. It moves away toward the higher elution volumes, for small molecular weights, owing to the increase in the aromaticity of the asphalt constituents as molecular weight decreases. It also moves away, and in the same direction, as the weight increases: in this case, molecular weight measurements lead to apparent values higher than the real values owing to the non-ideal behavior of the solutions. This difficulty may be overcome by accepting the hypothesis of the applicability of universal calibration to asphalt fractions and by using a viscosimetric detector to plot a new calibration curve with reference to the calibration curve in hydrodynamic volume. The interpretation of the results makes it possible to establish a calibration relationship of the form:  $\log M (\text{asphalt}) = 3.21 - 1.04 X + 0.331 X^2$ , in which X =  $\log M$  (polystyrene), and to elucidate, for asphalt fractions, the relationship between intrinsic viscosity and molecular weight.

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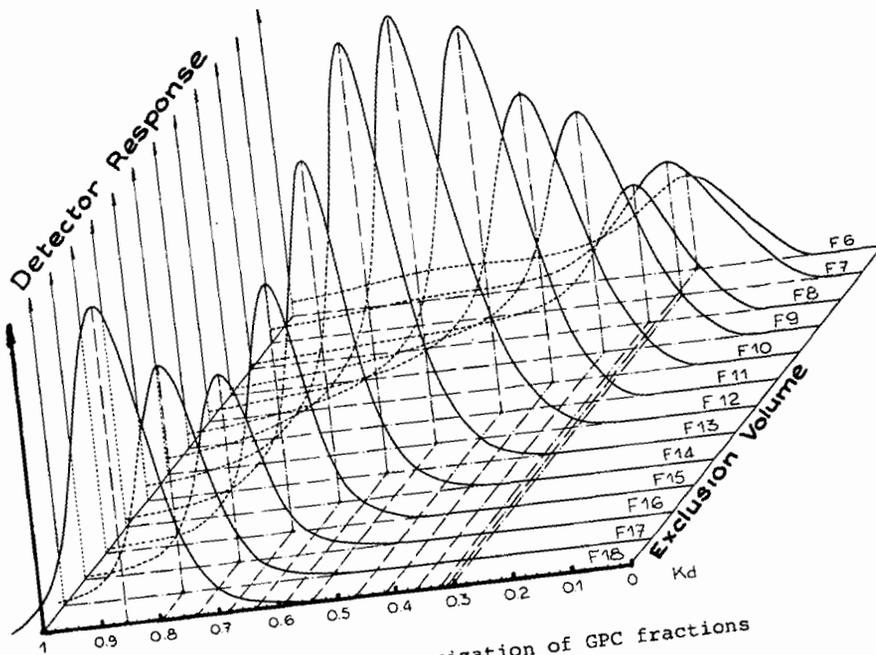


Figure 1. Characterization of GPC fractions

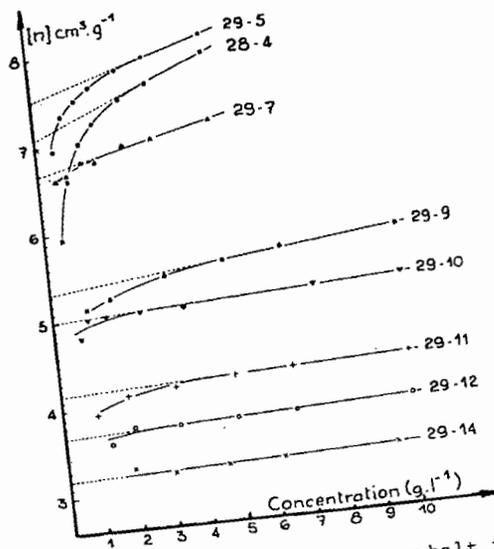


Figure 3. Viscosimetric curves for asphalt fractions

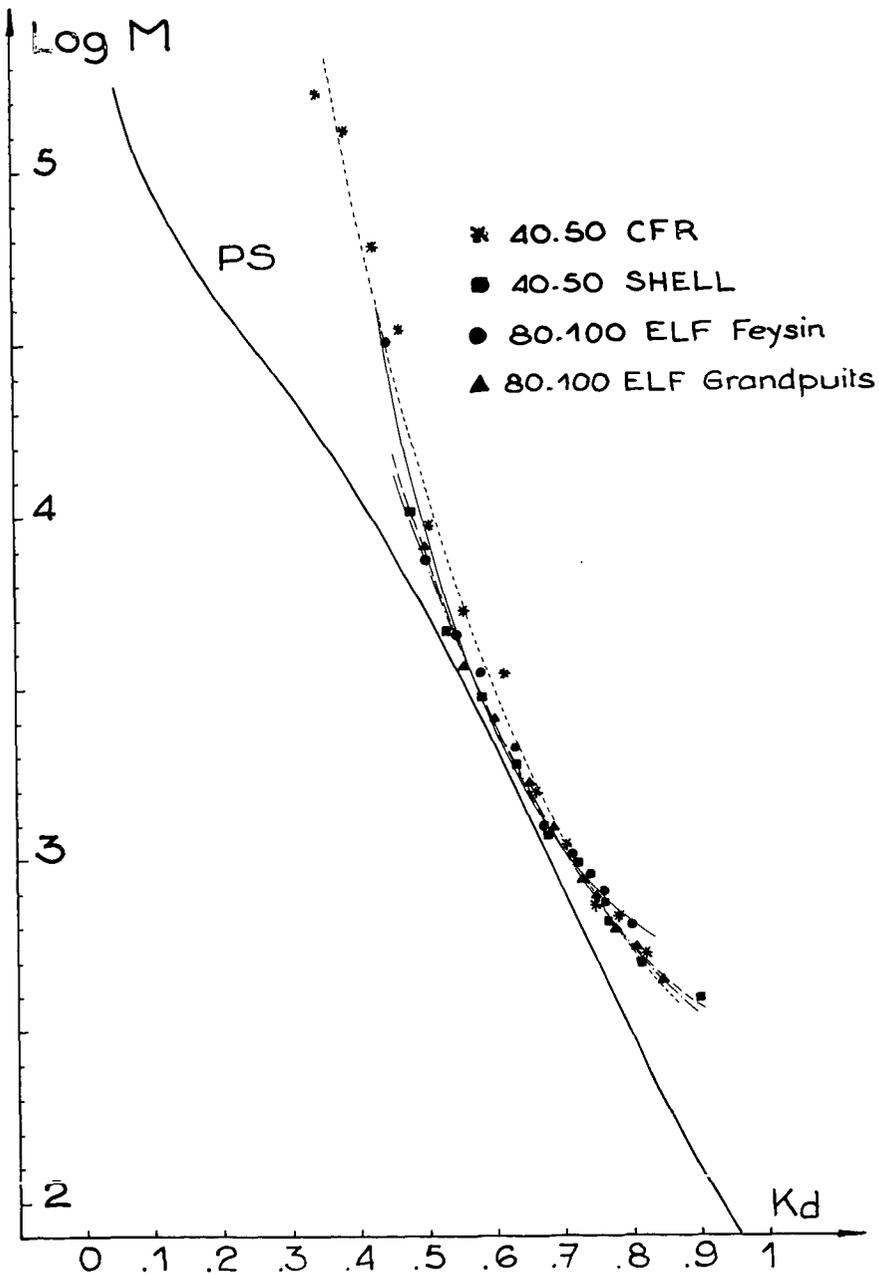


Figure 2. Calibration curve for asphalts by VPO and membrane osmometry

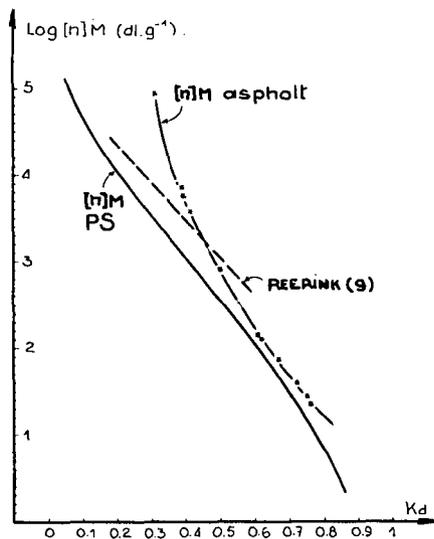


Figure 4.  $[\eta]M$  calibration curve for asphalt fractions

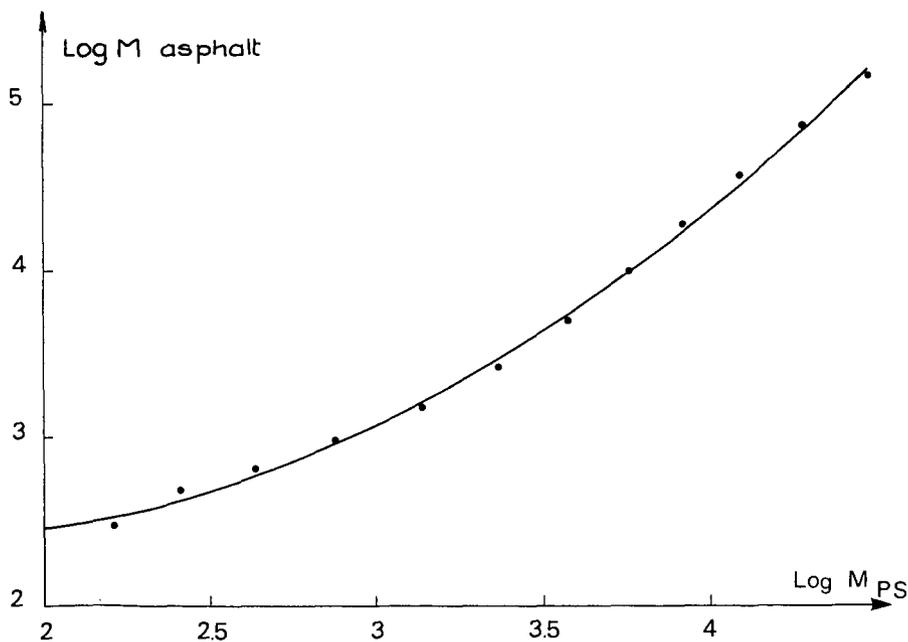


Figure 6. Relation between calibration curve for asphalt and calibration curve for PS

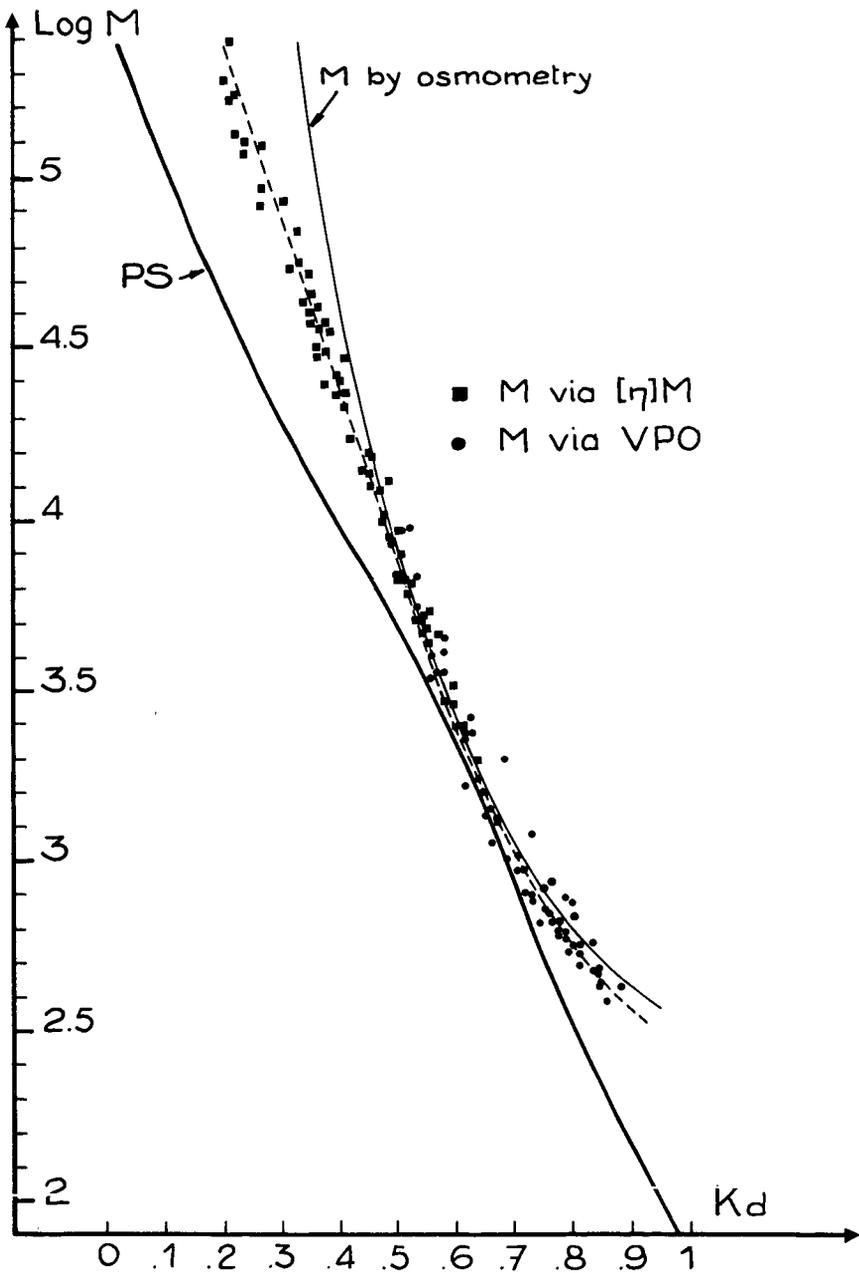


Figure 5. Calibration curve for asphalts from  $|\eta|M$

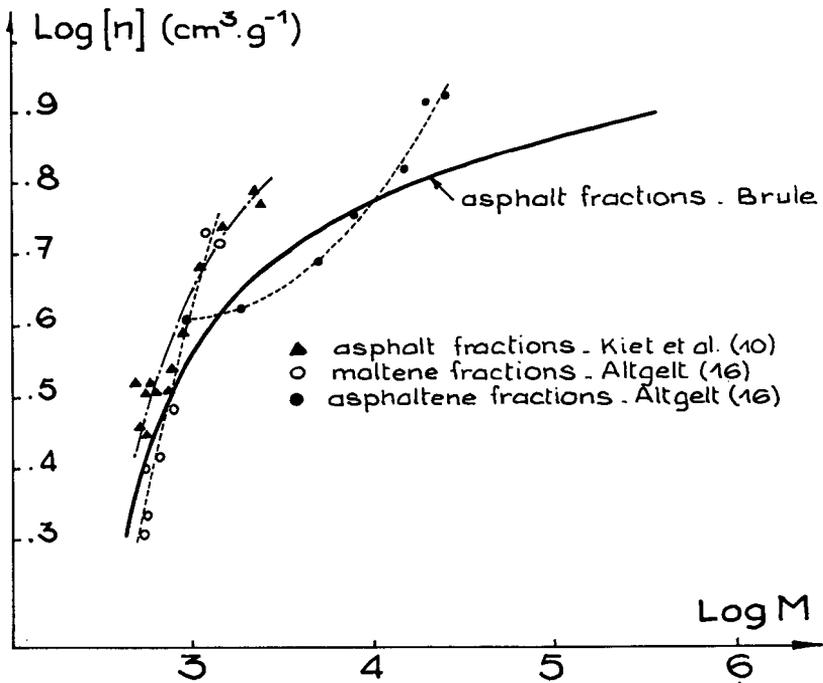


Figure 7. Relation between viscosity and molecular weight for asphalt fractions